

UDC 666.76

CARBON NANOTUBE REINFORCED CORUNDUM-BASED COMPOSITE MATERIAL

E. V. Zharikov,^{1, 4} K. S. Zaramenskikh,¹ N. A. Popova,¹ P. P. Faikov,¹
L. D. Iskhakova,² M. N. Gerke,³ S. V. Kutrovskaya,³ and D. S. Nogtev³

Translated from *Steklo i Keramika*, No. 3, pp. 12 – 16, March, 2011.

A new composite ceramic material based on corundum and reinforced with multilayer carbon nanotubes (CNTs) obtained by catalytic pyrolysis has been developed. Regimes for vacuum calcination and preliminary treatment of the initial mix have been determined; the compositions of the ceramic matrix, the concentration of the CNTs, and other technological parameters have been optimized. A uniform distribution of CNTs over the entire volume of the ceramic matrix has been achieved. As a result, a composite material with a reticular-framework structure of the CNT distribution showing a 1.5 – 2-fold increase of the cracking resistance has been obtained.

Key words: carbon nanotubes, corundum ceramic, vacuum calcination, composite material, reticular-framework structure, cracking resistance.

Carbon nanotubes (CNTs) are regarded as a promising strengthening material for creating composite materials due to the structural features of CNTs (the length/diameter ratio can reach several hundred), chemical inertness, and outstanding mechanical characteristics. The introduction of CNTs into ceramic makes it possible to improve substantially the existing properties of conventional ceramic structural materials [1 – 3]. The use of CNTs to reinforce ceramics based on corundum is of greatest interest. Corundum ceramic is the most common type of oxide ceramic, which because of the availability of the raw materials (alumina) and successful combination of mechanical, electrophysical, and chemical properties is widely used for manufacturing articles to be used in construction. According to the published data, when CNT⁵ are introduced into a composite material based on corundum ceramic in amounts less than 2.5 vol.% the plasticity of the ceramic samples increases and the bending strength also increases by more than 25% and the cracking resistance increases by 70% [4, 5].

However, there are a number of problems that limit the use of CNTs in ceramic. In the first place, it is difficult to

separate the bundles and attain a uniform distribution of the CNTs over the volume, and in addition the “slip through effect” arises because of poor binding of the nanotubes with the ceramic matrix. The slip through effect makes the mechanism of drawing fibers, which is responsible to increasing the cracking resistance of ceramomatrix composites, less effective. It should also be noted that the effect of carbon fiber structures on sintering and the microstructure of the material obtained has not been studied in detail.

The objectives of the present work are to develop a technology for the material Al_2O_3 – CNT and to study the effect of the conditions of calcination and concentration of CNTs on the microstructure and properties of the material.

The multilayer carbon nanotubes, ranging in diameter from 30 nm, used in the present work for implantation into ceramic material were obtained by catalytic pyrolysis of benzene at 980°C with the use of ferrocene as a precatalyst [6]. The CNTs were first treated in acids to remove particles of the catalyst and amorphous carbon impurities.

MgO-alloyed Al_2O_3 was used as the ceramic matrix. The addition of MgO, which is widely used in practice in the amounts 0.2 – 1.0 wt.% for preparing strong corundum articles, does not lower the sintering temperature, but it has a considerable effect on the crystallization of α - Al_2O_3 , slowing down grain growth, and also facilitates the acquisition of a more isometric shape by corundum crystals [7].

The mix for the ceramic matrix of the composite Al_2O_3 alloyed with 0.25 wt.% MgO to intensify sintering was ob-

¹ D. I. Mendeleev Russian Chemical Technology University, Moscow, Russia.

² Science Center for Fiber Optics of the Russian Academy of Sciences, Moscow, Russia.

³ Vladimir State University, Vladimir, Russia.

⁴ E-mail: zharikov@rctu.ru.

⁵ Here and below the CNT content in a composite is given in vol.%.

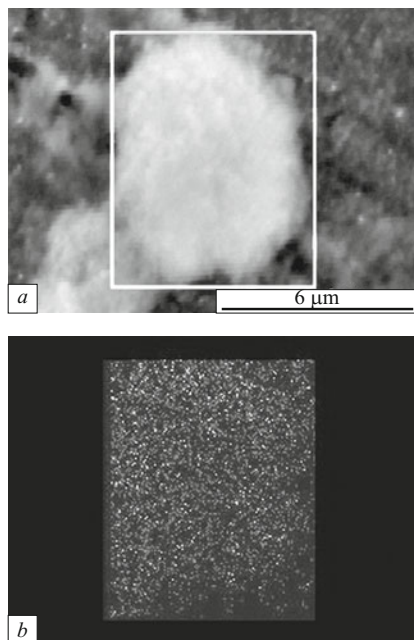


Fig. 1. Blank particle based on Al_2O_3 (alloyed with MgO), containing CNTs, on a Cu – Zn substrate: *a*) SEM image of the particle; *b*) map of the carbon distribution according to EDS data (the region of mapping is framed).

tained by solid-phase synthesis at 1100°C from aluminum chloride and magnesium nitrate and subjected to mechano-activation in a planetary mill. Carbon nanotubes were introduced in amounts up to 2 vol.% in the form of a suspension by pouring into the comminuted Al_2O_3 mix (with MgO added). To achieve effective separation of the bundles and a uniform distribution in the material the nanotubes are first dispersed by ultrasound (20 kHz) in ethanol with addition of sodium laureth sulfate (concentration 3 g/liter) as the surfactant.

Blanks were formed by semidry uniaxial pressing in the form of small beams with dimensions $40 \times 4 \times 4$ mm in a hydraulic press; the pressing pressure was 150 MPa. Ethanol, used for dispersing CNTs, gave the required moisture content in pressed powder. Different combinations of the concentrations of the CNTs introduced and the calcination regimes for the samples were used to obtain the composite. The calcination of the reinforced ceramic samples was performed in vacuum under residual pressure 10^{-4} mm Hg, varying the heating regime and the maximum calcination temperature in the range $1700 - 1730^\circ\text{C}$.

The microstructure of the samples obtained, the average particle size, and the character and the magnitude of the closed porosity were investigated by SEM — scanning electron microscopy (Jeol JSM-5910LV with the analytical system INCA ENERGY, QUANTA 3D 200), ACM — atomic force microscopy (Nterga Aura), and optical microscopy (“POLAM R-211”). The elemental composition of the samples was determined by energy-dispersion microanalysis (EDS).

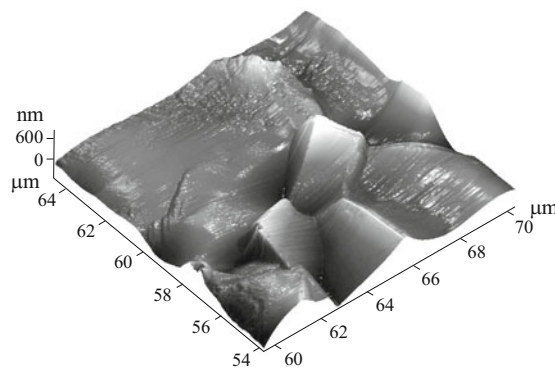


Fig. 2. Three-dimensional image (AFM) of individual crystals of nonporous composite Al_2O_3 (alloyed with MgO) – 0.1% CNTs.

The blanks obtained after mixing and pressing possesses a uniform distribution of carbon nanostructures over the volume of the material (Fig. 1).

A material without CNTs, characterized after sintering by $40 - 60$ μm isometric crystals and a unified closed porosity, was used as the comparison sample. The carbon nanotubes were introduced into the ceramic matrix in the following amounts: 0.1, 0.2, 0.5, 1, and 2 vol.%. The calcination of the samples was performed in three regimes: even heating to the final temperature with intermediate soaking at 1400°C for one or two hours and without soaking.

As the CNT content increases, the open porosity increases irrespective of the calcination regimes (from 0.4% for a sample without CNTs to 3.6% for a sample with 2% CNTs), which is due to the presence of CNTs in the composite material, since even though the corundum matrix is completely sintered, the hollow channels inside and between the CNTs remain. As the CNT content increases, the linear shrinkage of the sample during sintering decreases stably (from 27.2 to 23.6%, respectively) also irrespective of the calcination regime. This phenomenon shows that for high-temperature calcination nanotubes remain in the volume of the ceramic matrix and impede densification of the material during the shrinkage process.

The necessity of intermediate soaking at 1400°C during sintering to eliminate closed porosity was determined on the basis of studies of the microstructure and ceramic properties of the sample of composite material obtained. Figure 2 displays an AFM image of a cleavage face of a sample containing 0.1% CNTs, which was obtained by sintering at 1700°C with soaking for 2 h. The sample possesses zero closed porosity with close intergrowth of grains, and the typical size of the isometric crystals of the matrix is $8 - 12$ μm.

As the CNT content increases, the recrystallization process in the material intensifies, which results in larger crystallites of the Al_2O_3 matrix. As Fig. 3 shows, in a sample containing 1% CNT (obtained in the same calcination regime as the preceding sample) the matrix consists of Al_2O_3 crystals with average size $12 - 20$ μm. The structure of the CNTs remains the same, but they do not reinforce the structure of

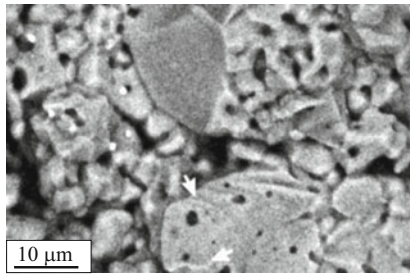


Fig. 3. Ceramic sample (SEM) containing 1 vol.% CNTs; the nanotubes (light colored lines marked by arrows) are distributed predominately inside the crystals.

the Al_2O_3 grains, rather they become distributed predominately inside crystals in the form of bundles, which an investigation of the material in transmitted light showed. For the entire series of samples of the composite material, bundles of nanotubes with diameter from 0.5 to 4 μm are characteristic but in some places the diameter reaches 10 μm or more.

The high sintering activity of the material obtained by solid-phase synthesis resulted in substantial growth of the crystals, so that for further investigation of the method of introduction and the concentration of CNTs the technology used to prepare the mix was modified. Aluminum hydroxide and magnesium hydroxo-carbonate were used as the initial reagents; the charge was first soaked at 1300°C for 1 h, which made it possible to lower its sintering activity, obtaining isometric and crystallographically more perfect grains of the mix. The content of MgO was increased to 0.5 wt.% to decrease the recrystallization. High-temperature vacuum calcination of the samples in this series was performed according to a regime developed on the basis of the preceding data to final temperature 1700°C with intermediate soaking at 1450°C for 2 h (Table 1).

The sample with no CNTs contains, among large crystals with ideomorphic shape 60 – 80 μm , a polycrystalline mass consisting of Al_2O_3 with 8 – 12 μm crystals. The closed porosity of the material is an individual porosity in the form of separate intercrystalline pores up to 5 μm in size.

The structure of the sample obtained by introducing 0.05% CNTs is similar to the preceding case. The large crystallites range in size from 40 to 70 μm ; the fine grain mass, which comprises these ideomorphic grains, is of the same

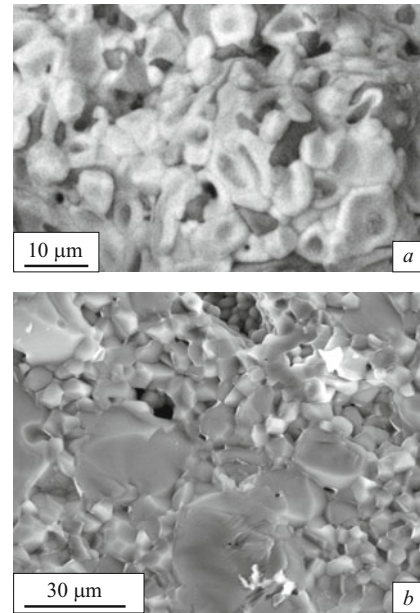


Fig. 4. Ceramic samples with equal-crystallite block structure, which were obtained from mix deactivated at 1300°C with CNT content: a) 0.1 vol.%; b) 0.2 vol.%.

size. The CNT bundles ranging in size to 4 μm are rare, and a reinforced structure is not observed.

Starting with CNT content 0.1% a more uniform distribution of the CNs is observed as a result of the increase in the total number of their bundles, also up to 4 μm in size. The bundles of nanotubes in the material form a three-dimensional reticular structure, which is clearly seen under an optical microscope with transmitted light. Complete intergrowth of the corundum matrix and absence of a characteristic intracrystalline porosity not due to the presence of CNTs is observed (Fig. 4a).

The sample containing 0.2% CNT has an equal-crystallite structure consisting of differently oriented blocks. The size of the crystals inside the blocks is 6 – 8 μm , and the blocks along whose edges a reticular CNT structure forms range in size from 35 to 40 μm . The diameter of the CNT blocks increases and reaches, on average, 5 – 6 μm (Fig. 4b).

Thus, when mixes obtained from aluminum hydroxide and magnesium hydroxocarbonate are used, preliminary soaking at 1300°C and new calcination conditions result in

TABLE 1. Characteristics of Ceramic Samples Obtained from Al_2O_3 Mixe (0.5% MgO) Heat-Treated at 1300°C (Mixing with CNTs by Pouring)

Sample	CNT content, vol.%	Linear shrinkage, %	Apparent density, g/cm ³	Porosity, %		Size of crystals/blocks, μm
				open	closed	
1	0	19.4	3.84	0.4	< 0.1	8 – 12/60 – 80
2	0.05	19.2	3.76	0.3	< 0.1	8 – 12/40 – 70
3	0.10	18.5	3.69	0.4	< 0.1	8 – 10/40 – 50
4	0.20	19.8	3.65	1.5	–	6 – 8/35 – 40

CNTs distributed along crystal grains and in decreasing sizes of individual crystals and blocks of the Al_2O_3 matrix material with increasing CNT content.

To obtain a more effective separation of the CNT bundles and improve the CNT distribution in the corundum matrix Al_2O_3 (0.5 wt.% MgO) the charge was mixed with CNTs in a planetary mill with ethyl alcohol as the medium, which ensured, on the one hand, more effective mechanoactivation and, on the other hand, a more uniform CNT distribution. The samples obtained in this way (in contrast to the preceding series, where the blanks became darker as the CNT concentration increased) had the same color (all white) depending on the CNT content, indicating a more uniform nanotube distribution over the volume of the sample and separation of the CNT bundles into smaller bundles. Vacuum calcination of the samples of the composite material from series was also performed at 1700°C with soaking at 1450°C for 2 h.

The structure of the corundum material without the addition of CNTs is coarse-crystalline and nonuniform; the size of the crystallites varies from 20 to 80 μm . The in- and intercrystalline pores are 3 – 4 μm in size and the total closed porosity is up to 3% (Table 2).

With the introduction of 0.05% CNT the size of the crystallites decreases and, on average, is in the range 16 – 35 μm . Compared with the samples obtained by dry milling (see Table 1), a more uniform CNT distribution in the volume was obtained, and the tubes create a reticular-framework structure. The diameter of the CNT bundles is 1 – 4 μm . Since the CNTs are distributed around corundum grains, they impede the growth of crystals in this case.

The crystals of the material containing 0.1% CNT are even smaller, since the nanotubes impede the growth of crystals more strongly. The fibers retain their structure, creating a closed intercrystalline porosity in the form of a reticular structure. The diameter of the CNT bundles ranges from 2 μm upwards.

The size of the crystal in material containing 0.2% CNT is 8 – 16 μm . The crystals adjoin one another closely, and CNT bundles are located along their periphery (Fig. 5). The closed porosity of the ceramic itself is about 0.5%, and the remaining closed porosity is a pore structure due to the presence of CNTs, forming a reticular framework along the pe-

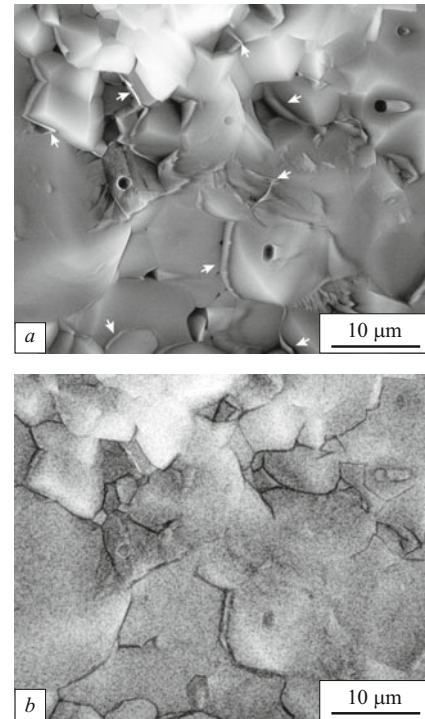


Fig. 5. Ceramic sample Al_2O_3 (alloyed with MgO) with 0.2 vol.% CNT addition obtained from the mix deactivated at 1300°C and mixed in ethanol medium: a) SEM image; b) graphically transformed photograph with accent on the location of the CNT bundles (marked in black) along the periphery of the corundum grains.

riphery of the corundum grains. The size of the CNT bundles mainly ranges from 1 μm upwards.

In summary, with comminution and mixing in ethanol as the medium we obtain finer CNT bundles which are stable and uniformly distributed in the volume of the material, irrespective of the dependence on the CNT concentration introduced. The nanotube bundles create a reticular-framework structure along the periphery of the corundum grains after heat-treatment in vacuum and facilitate removal of the closed intercrystalline porosity, drawing individual pores to itself. For the subsequent series of samples, the magnitude of the crack stability was measured by the method of indentation. The results showed that the maximum value $K_{Ic} = 6.4 \pm 0.2 \text{ MPa} \cdot \text{m}^{1/2}$ is attained for a sample of the composite material containing 0.2% CNT.

TABLE 2. Characteristics of Ceramic Samples Obtained from Al_2O_3 Mix (0.5% MgO Added) Heat-Treated at 1300°C (Mixing with CNTs in a Planetary Mill in Ethanol as the Medium)

Sample	CNT content, vol. %	Linear shrinkage, %	Apparent density, g/cm ³	Porosity, %		Crystal size, μm	K_{Ic} , MPa · m ^{1/2}
				open	closed		
1	0	24.5	3.93	< 0.1	3.0	20 – 80	3.2 ± 0.2
2	0.05	24.2	3.93	< 0.1	< 0.1	16 – 35	–
3	0.10	24.5	3.94	< 0.1	< 0.1	8 – 20	5.2 ± 0.2
4	0.20	24.1	3.93	< 0.1	< 0.5	8 – 16	6.4 ± 0.2

So, in these investigations a composite material based on corundum reinforced by carbon nanotubes was obtained and a technological mixing process making it possible to obtain a uniform distribution of carbon nanotubes over the volume of the corundum matrix was developed. In addition, the calcination regimes, the volume content of CNTs, the composition and the preliminary treatment of the initial mix were optimized, which made it possible to obtain a denser composite with CNTs arranged along the grain boundaries of the ceramic matrix and to avoid embedding of CNTs into the structure of the growing crystals.

The CNT bundles along the periphery of the corundum grains remain in the volume matrix and impede crystal growth provided that high-temperature calcination is performed.

As a result, a structure of the composite material with reticular-framework distribution of CNTs has been obtained. This improves the structure of the matrix and increases the cracking resistance 1.5 – 2-fold.

REFERENCES

1. O. Lourie, D. M. Cox, and H. D. Wagner, "Buckling and collapse of embedded carbon nanotubes," *Phys. Rev. Lett.*, **81**(8), 1638 (1998).
2. M. R. Falvo, G. J. Clary, R. M. Taylor II, "Bending and buckling of carbon nanotubes under large strain," *Nature*, **389**(6651), 582 – 584 (1997).
3. Ya. I. Guzman (ed.), *Chemical Technology of Ceramics* [in Russian], Moscow (2003).
4. G. Yamamoto, M. Omori, T. Hashida, and H. Kimura, "A novel structure for carbon nanotube reinforced alumina composites with improved mechanical properties," *Nanotechnology*, No. 19 (2008).
5. Naoki Ueda, Tomohiko Yamakami, Tomohiro Yamaguchi, et al., "Fabrication and mechanical properties of high-dispersion-treated carbon nanofiber/alumina composites," *J. Ceram. Soc. Jpn.*, **118**(9), 847 – 854 (2010).
6. X. Devaux, S. Yu. Tsareva, A. N. Kovalenko, et al., "Formation mechanism and morphology of large branched carbon nanostructures," *Carbon*, **47**, 1244 (2009).
7. V. L. Balkevich, *Technical Ceramics* [in Russian], Stroiizdat, (1984), 2nd edition.